Surface Engineering of Nanomaterials
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Lecture - 15
Advance of Deposition for Surface Modification

Hello. Today we are going to start our new lecture on Advantages of Depositions for Surface Modifications. In our last lecture we have discussed about the different types of surface modification techniques, generally those are the nonconventional or maybe the unconventional methods. Before that we have discussed about the PBD physical vapour deposition, then after that we have done with the chemical vapour deposition and then last lecture we have discussed about the different types of some unconventional modification methods.

Today, actually we are going to discuss those unconventional or may be the conventional modifications where we are going to use, what are the applications of those modifications. So first we have to see that; what are the advantages of depositions in different areas?

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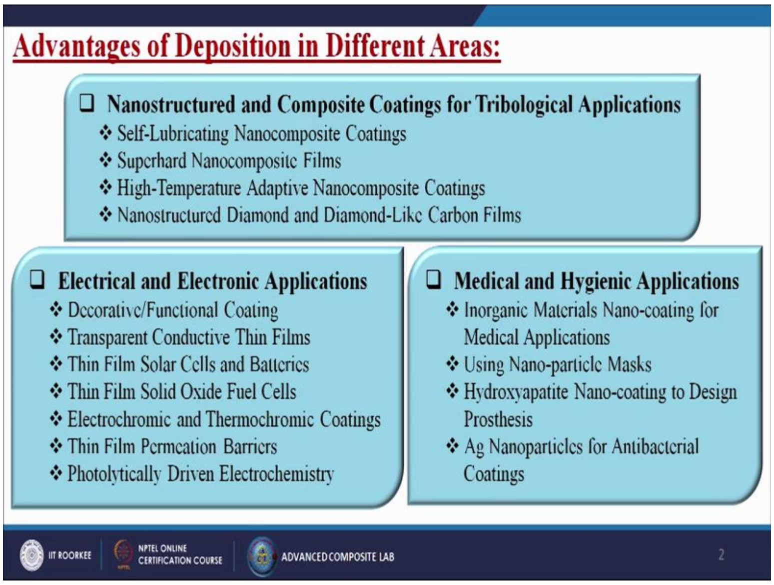

In last couple of lectures I have discussed about what are the problems, that why you are going to do the surface engineering. We have faced certain problems about where we have faced certain problems about abrasions. Then we are trying to do the surface modifications by the conventional methods. Then after that we have we are trying to do the modifications into some nano levels, but in this particular lecture we are going to discuss about the nano level applications where we are going to do the surface modifications.

So, first we will start with the nano structure and composite coatings for the tribological applications. So, here the main criteria are that tribology. So, we want to recover the wear and abrasion problems of certain particular materials. We want to make the surface modifications and to strengthen its life. So, first is we are doing that self lubricating nanocomposite coatings, then superhard nanocomposite films, high temperature adaptive nanocomposite coatings and nanostructure diamond and diamond like carbon plane. So, these all are the applications are best on tribological application. So we are here, we are going to see that we are going to do different types of modifications by which we can modify the tribological properties of that particular material.

Next, we are going to discuss about the electrical and electronic applications, like decorative or functional coatings, transparent conducting thin claims, thin film solar cells and batteries, thin film solid oxide fuel cells, electrochromic and thermochromic coatings, thin film permeation barriers, photolyticallyy driven electrochemistry. So, these all are the related with that electronic application where we are going to modify the electrical properties of those particular materials by doing different types of coating.

And next we are going to discuss about the medical and hygienic applications where we will discuss about the inorganic materials nano-coating for medical applications using nanoparticle mask, hydroxyapatite nano-coating to design processes, silver nanoparticles for antibacterial coatings.

So, first we are going to discuss the materials which will help us on that tribological aspect. So, first thing is that it is known as the self-lubricating nanocomposite coatings.

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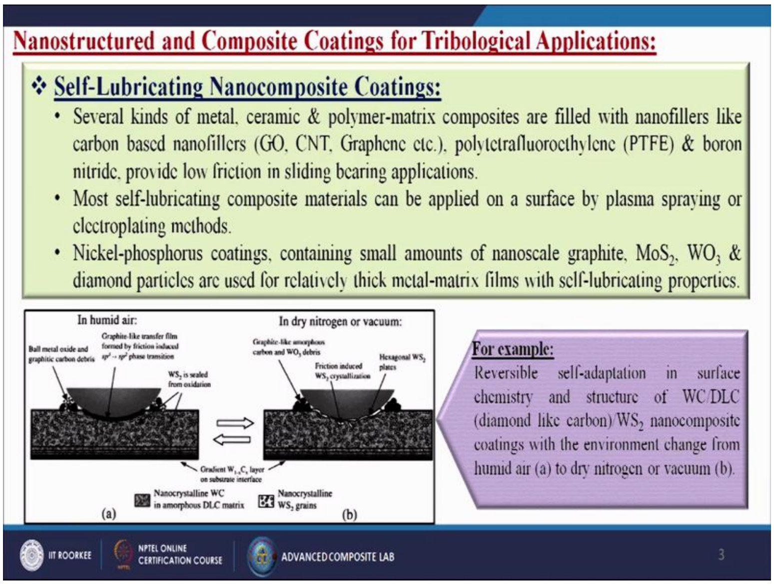

In my several lectures I have discussed that there are certain materials which can act as a self lubricating. So, when those materials we are incorporating into some matrix or into some composites into some blends or alloys, so after preparation that material can itself self lubricate and can self put any kind of a barrier so that any materials or maybe the environment cannot attack directly to them.

Here are the examples like grapheme, oxide carbon nanotubes, graphene are those kinds of materials. So, here we are giving the examples like several kinds of metals and ceramic and polymer matrix composites are filled with nanofiller, like carbon based nanofillers generally the carbon based nano pillars are having that inner end property that it can sell lubricate itself. It can acts as a self lubricating material. So, poly tetra fluoro ethylene PTFE, boron nitride, provide no friction inside the sliding bearing application.

So the means is that, where we need the less friction less operations less wear in that particular cases we can think of for using these kinds of materials so that automatically the friction in sliding bearing applications will be reduced. Most self lubricating composite material can be applied on a surface by plasma spring or electroplating methods. Nickel phosphorous coatings containing small amount of nanoscale graphite, molybdenum sulfide, tungsten oxide. And diamond particles are used for relatively thick metal matrix with self lubricating properties. So, these are the materials where we can do the mixing with some matrix and it can act as self lubricating materials.

So, here we are giving one small examples based on some literature survey. So, like reversible cell adaptations in surface chemistry and structure of tungsten carbide. And DLC is nothing but the diamond like carbon with tungsten sulphide nano composite coating with the environment change from humid air to dry nitrogen or vacuum. So a is giving you the humid air conditions and b is giving you the dry nitrogen or the vacuum. That means, we are developing certain materials which can acts as a self lubricating in the humid conditions as well as into the dry medium to, because as a material scientist when we are developing certain material we do not know where the material will be applied.

We are having a rough idea or maybe the broad area, but we do not know the specific working or temperature range for those particular materials; may be that materials can be used in the minus temperature or maybe some humid conditions or maybe some dry conditions. So, we have to add up certain kind of coating techniques or maybe the coating materials which can act in the humid air conditions or into the dry air conditions or maybe the dry nitrogen or vacuum conditions too.

Next we are going to discuss about some super hot nanocomposite flims. So, basically this kind of coatings we are using for some kind of cutting tool materials, some kind of materials which where we need the maximum strain maximum load bearing capacity and the material should be super hard. That means, it should not be corrode, there should not be any scratch or maybe any kind of rupture can occur on to that particular material.

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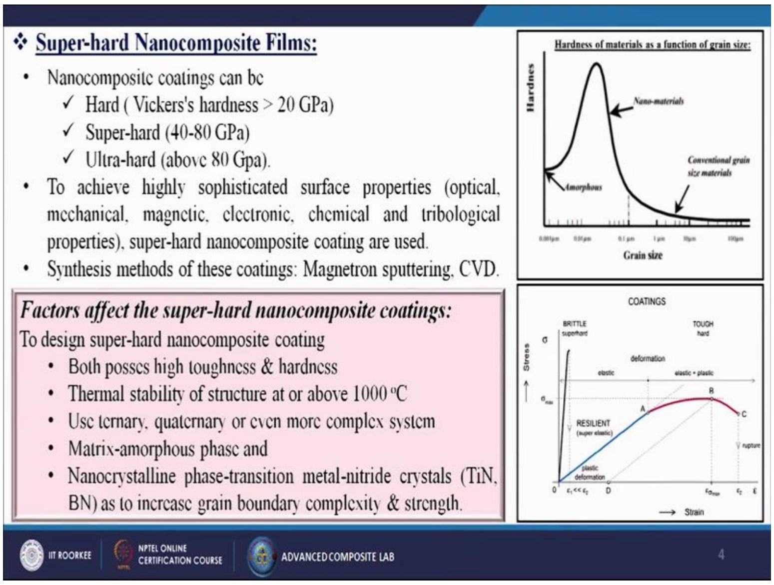

So, nano composite coatings can be hard when the Vickers's hardness is more than 20 Giga Pascal. Super hard generally when it is around 40 to 80 Giga Pascal and ultra hard is above 80 Giga Pascal. That means, based on the mechanical strength or main based on the hardness which we are achieving from that particular materials we can divide the material into different zone; that is like hard super hard or maybe the ultra hard.

To achieve highly sophisticated surface properties like optical, mechanical, magnetic, electronic, chemical and tribological properties super hard nanocomposites coatings are used; synthesis method of these coatings magnetron sputtering or maybe the chemical vapour deposition techniques, so by these techniques we can do the coating of this kind of materials.

Factors affect the super hard nanocomposite coatings. To design super hot nanocomposite coatings both process high toughness and hardness, thermal stability of structure at or above 1000 degree centigrade, use ternary quaternary even more complex systems, matrix amorphous phase and nanocrystalline phase transition metal nitride crystals like titanium nitride boron nitride has to increase grain boundary complexity and strength. That means, depending upon our requirement that what properties we need maximum or what property we want to get from that particular material we have to choose the different coating materials and also that different coating techniques.

So here, in the right hand side we have given certain example that when we are talking about the hardness and the grain size we have seen that 0.001 micrometer is achieved when the material is into the amorphous region, but its hardness is low. But when the grain size is ranging from 0.01 micrometer to 0.1 micrometer we are calling it as a nano materials and the hardness is maximum. That means, when we are using the particles into the nano size automatically its properties is getting increased.

Then, the conventional grain size material is beyond 1 micrometer. And here also we have given one examples about the coatings. See for the super hard materials the stress or maybe the tensile properties will be maximum but it will be the brittle in nature and it is known as the super hard. But when there will be some elastic properties into that particular material, so automatically it is brittleness will be decreasing but its elasticity will be increasing. So, automatically the ductility of that particular material will be increasing. So, the material will be little bit softer.

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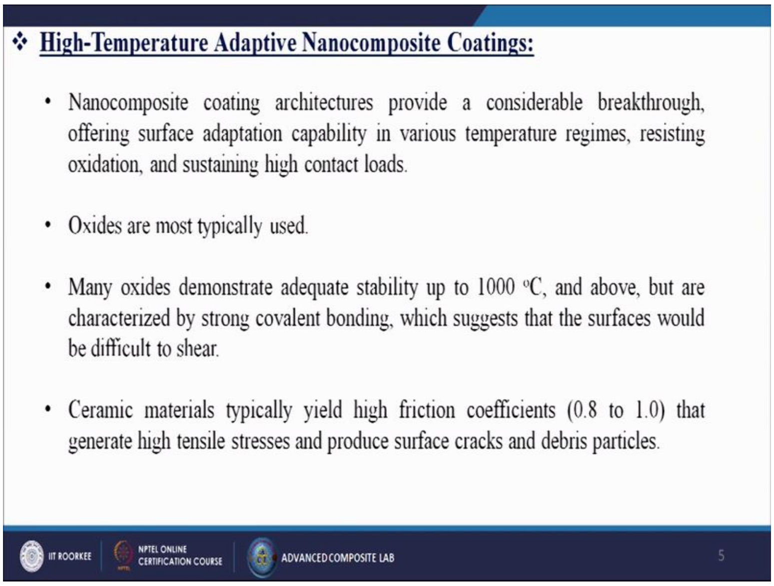

Then we are going to discuss about the high temperature adaptive nanocomposites coatings. This is also one type of new methods by which we can improve the surface properties of particular materials. Nanocomposite coatings architects provide a considerable breakthrough offering surface adaptation capability in various temperature regimes, resisting oxidation, and sustaining high contact loads. Actually, if we see in more precisely we can find that these are the reasons for which we are going to do these kind of coatings onto the materials all rather onto the nano materials. Because till now we have discussed about the macromolecules or maybe the some kind of surface, but in this particular case we are discussing about some materials which are into the nano size.

So, oxides are most typically used many oxides demonstrate adequately stability up to 1000 degree centigrade and above, but are characterized by strong covalent bonding which suggests that the surface would be difficult to shear. Means, the lubricating properties of that particular material is going down so it is become a little bit dry, so friction will be more. Ceramic materials typically yield high friction coefficients generally 0.8 to 1.0 that generate high tensile strength and produce surface cracks and debris particles.

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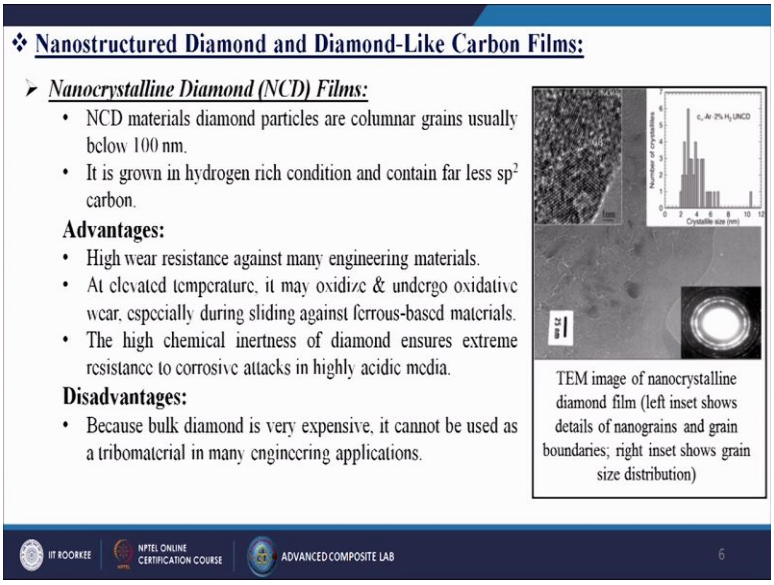

Now, we are going to discuss about the nanostructure diamond and diamond like carbon films. Here, nowadays people are working on the carbon nanotubes, people are working on the graph in or maybe that graph in quantum dots or maybe the nanoribbons, but though our requirement is getting high and high so people are trying to do the modification of those nanofillers too.

So, we are trying to do the modifications of this kind of films that is known as the nanocrystalline diamond films. So, NCD materials diamond particles are columnar grains usually below the 100 nanometer. It is grown in hydrogen rich conditions and contains far less sp 2 carbon. What are the advantages? High wear resistance again many engineering materials, at elevated temperature it may oxidize and under oxidative wear, especially during sliding against ferrous waste materials. The high chemical inertness of diamond ensures extreme resistance to corrosive attacks in highly acidic media.

So, suppose we need to enhance this kind of properties or maybe certain properties in terms of some thermal properties or mechanical properties then we can think about this kind of materials. So, what are the disadvantages, because bulk diamond is very expensive it cannot be used as a trim material in many engineering applications is of course. But still people are using this kind of diamonds which is artificially made into the laboratory itself, and it is not the diamond which generally we are using for the ornamental purpose it is the some diamonds which is having the high impurity. So that materials can be used for these kinds of modifications.

And the right hand side we are going to show you some kind of tame image of this nanocrystalline diamond film. So, where in inside we are showing some kind of nanograins over there and some kind of grain boundaries and right inside shows the grain size distributions. So, the particle size is generally ranging from 2 to 7 maybe in between 6 or 8 maybe roughly we can say it as a 7, so in between 2 to 7 nanometer range. So, that is the rough average diameter of those nanocrystalline diamonds.

Next, we are talking about the nanostructured carbide derived carbon coatings. So, this is also one kind of latest modifications generally we are doing for various applications.

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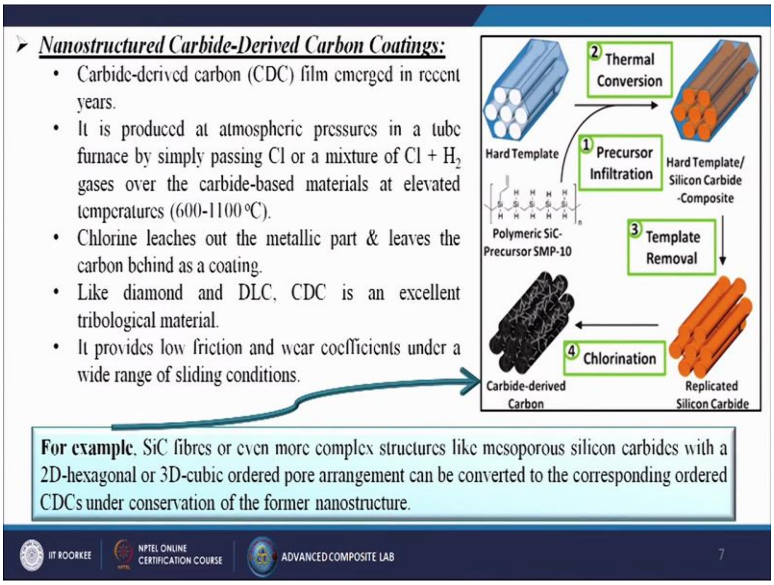

The carbide derived carbon film emerged in recent years. It is produced at atmospheric pressure in a tube furnace by simply passing chlorine or a mixture of chlorine and hydrogen gases over the carbon based materials at elevated temperature generally temperature is ranging from 600 to 1100 degree centigrade. Chlorine reaches out the metallic part and leaves the carbon behind as a coating. Like diamond and DLC, CDC is an excellent through biological materials.

So, the thing is that chlorine and hydrogen both we are passing on to the substrate. The chlorine it will be deposited on the substrate and hydrogen it will automatically go out, so there will be a coating of the carbide onto the materials. It provides low friction and wear coefficient under a wide range of sliding conditions. So, right hand side all are the examples, like silicon carbide fibers or even more complex structures like mesoporous silicon carbides with a 2-D hexagonal or 3-D cubic or that pore arrangement can be converted to the corresponding orders CDCs under conservation of the format nanostructure.

So, here we are taking first the precursors then we are doing the thermal conversions over there then hard template silicon carbide is forming then we are removing those templates and then we are doing the chlorine nations, so that removing of the chlorine on the surface then we are getting the carbide derived carbon materials. So, like this way we are modifying those nanoparticles.

Next is that nano composites DLC film.

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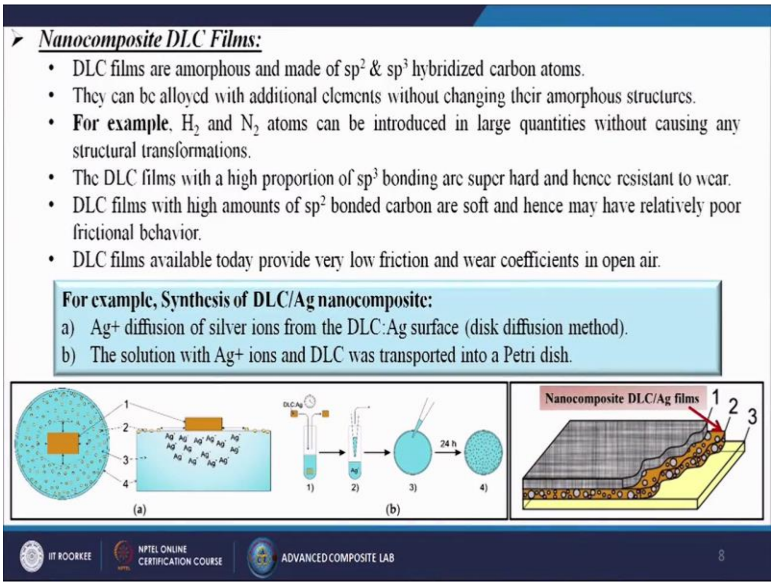

So, last slide we have discussed about the how we are going to do the coatings of those nanoparticles. Now in this particular slide we are going to discuss about how we are using those nanoparticles for making any kind of products or maybe the materials. So, DLC films are amorphous and made of sp 2 and sp 3 hybridized carbon atoms. As already I have discussed. They can be alloyed with additional elements without changing they are amorphous structures. For example, hydrogen and nitrogen atom can be introduced in large quantities without causing any structural transformations.

So, we are not going to change the whole material properties rather bulk material properties just we are trying to change the surface properties of that materials so that we can get the better surface properties. The DLC films with a high proportion of sp 3 bonding are super hard and hence resistant to wear. DLC films with high amounts of sp 2 bonded carbon are soft and hence may have relatively poor frictional behavior. DLC films a available today provide very low friction and wear coefficient in open air. That is the most vital applications of this DLC film.

For example, we have given certain example; here is the a and this is the b. So, a is the silver and diffusion of silver ions from the DLC Ag surface, this diffusion methods. Here we are putting the materials so that the silver ion is going inside the materials. Then the solutions with Ag plus ions of DLC were transported into the Petri dish. And like broadcasting methods we are putting that material into the Petri dish and we are drying and we are doing the materials like this. So this is the 1, this is the 2 and this is the 3. So, here is the 1, 2 and 3. So finally, we are getting the structure like this. So, it is a layer by layer structure it is forming.

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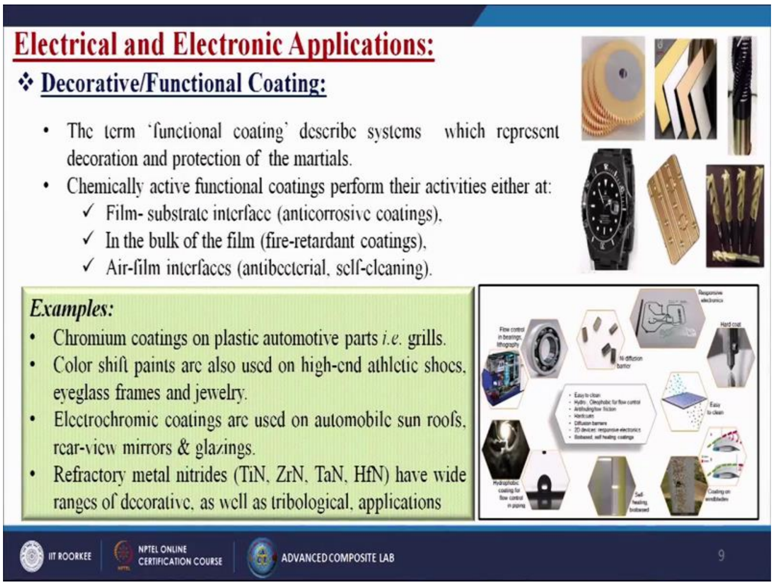

Next, we are discussing the materials where that material can be used for the electrical or maybe the electronic purposes. So, first is called the decorative and functional coatings. So, right hand side picture from this picture you can see that, here we are doing this kind of coatings for our watch for our ornaments or maybe some kind of expensive jewelry or maybe some kind of tools, so that it can be hardened so that its material removal rate will be higher.

So, the term functional coatings describe systems with represent decorations and protection of the materials. Chemically active functional coatings perform their activities either at: film substrate interface anticorrosive coatings, in the bulk of the film fire retardant coating, air film interface antibacterial and self cleaning. Here, these all of the applications for antibacterial applications, anti corrosion applications, then fire retardant materials, here for applying for getting these properties we can do these kind of coatings.

What are the examples? Chromium coatings on plastic automatic parts generally we are using for the grills for the automotive or maybe somewhere nowadays we are seeing that the plastics, but it is growing like nickel or maybe the stainless steel. So, that is the beauty of these decorative and functional coatings. Color ship paints are also used on high-end athletic shoes, eyeglass frames and jewelry. Electrochromic coatings are used on automobile sun roofs, rear-view mirrors, glazing's. So, that the sunlight not barely come into inside the car or maybe not directly fall onto the drivers eye or something like that. And heat also it will not be absorbed inside the automotive car.

Then, refractory metal nitrites like titanium nitride, zirconia nitride, tantalum nitride, hafnium nitride, have wide range of decorative as well as tribological applications. Here we have given certain examples that where we are going to use this kind of materials. So, we are using these materials for the bearing applications, where we are using some materials for the electronic applications, we are doing it for the hard coat for any making any indentations on to the any kind of materials. Then we are going to use these kinds of coatings for the window glasses. Then self healing materials then we can make these materials for the hydrophobic in nature from the hydrophilic. And then there are several kinds of applications are listed over there which we can do by these kinds of coatings.

Then we are going to use these coatings for the transparent conducting thin films. So, here transparent conducting coatings and transparent conducting oxide have a wide range of optical device photovoltaic energy and display applications. Nowadays we are doing these coatings on our glasses so that any kind of a light or maybe the computer rays not directly come into our eyes it can be reflected. Not only that we are using these kinds of coatings on the windshield or maybe that automotive car front mirror or maybe the side mirror so that the opposite side headlight that not directly come into the drivers eyes. Or maybe we are using these kinds of coatings onto some glass windows maybe doors. So, there are lots of applications. Also this kind of materials we are using for the electronic purpose, making some kind of semiconducting materials or maybe some kind of optoelectronic materials.

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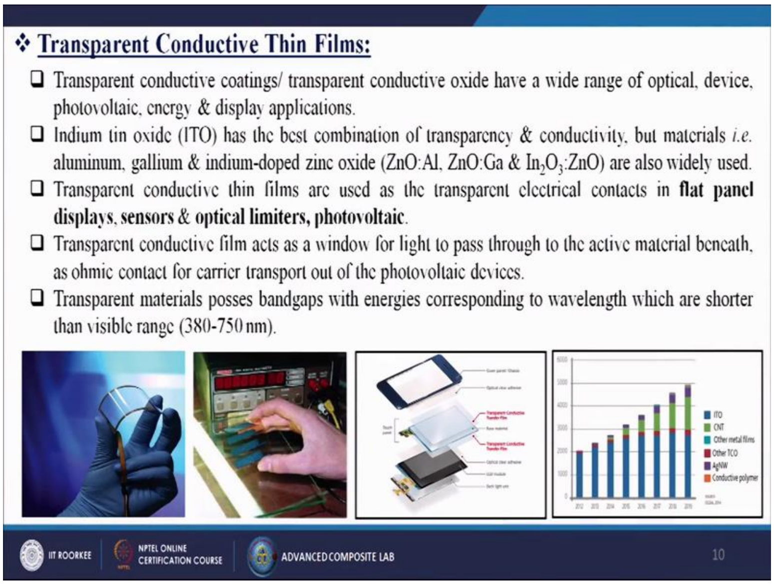

So, what are the examples? Indium tin oxide has the best combination of transparency and conductivity, but materials, aluminum, gallium, indium dog zinc oxide are also widely used. So, these all are the letters materials which we are using for some kind of transparency and conductivity operations.

Transparent conductive thin frames are used as transparent electrical contacts in flat panel displays, sensors optical limits, photovoltaic, solar cells, so there are lots of applications of this kind of materials. Transparent conductive films acts as a window for light to pass through to the active material minute as ohmic contact for carrier transport out of the photovoltaic devices. Transferring materials processes bandgaps with energies come corresponding to air blends which are shorter than the visible range. That means it is in the range of 380 to 750 nanometer. So, here the application is for the electronic purposes.

So, now we are discussing about the thin films which are using for the solar cell applications and the batteries applications. Nowadays people are talking about the lithium ion battery and some kind of solar cells like dye sensitized solar cells or maybe the pool of peroxide solar cells, so there are lots of applications.

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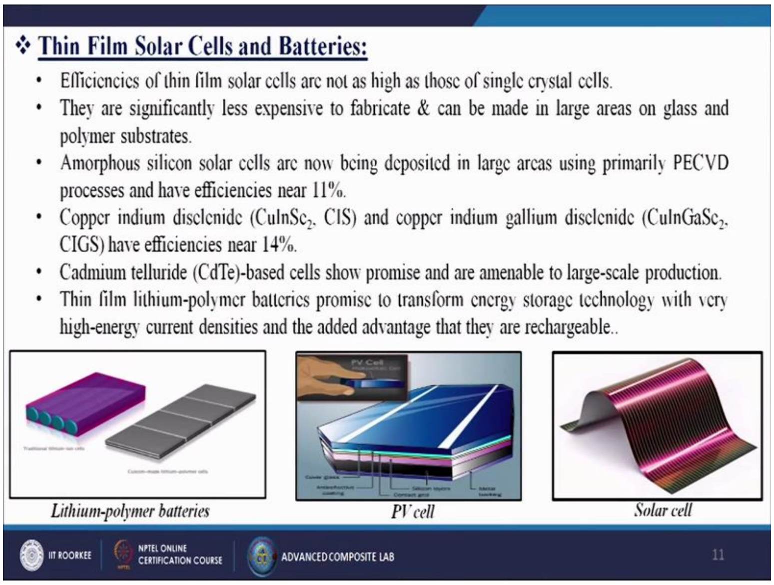

So, here generally what we are doing, efficiencies of thin film solar cells are not as high as those of single crystal cells. They are significantly less expensive to fabricate and can be made in large areas on glass and polymer substrates. Amorphous silicon solar cells are now being deposited in large areas using primarily PECVD process and have efficiencies near 11 percent.

So, the main drawback of making any kind of solar cells is the efficiency. So, people are or maybe the scientist or maybe the researchers are trying to enhance the efficiencies of these solar cells by using this kind of coating by using different types of materials to enhance its efficiency level. So, copper indium diselenide and copper indium gallium diselenide have efficiencies near 14 percent. So, you see that we have reached from 11 percent to 14 percent just doing this kind of thin film materials or maybe just researching on these thin film materials. Cadmium telluride best sells show promise and are amenable to large scale productions.

So, here all are the examples where we are using for the lithium polymer batteries for our mobiles, for our laptops, for our iPad's or maybe the iPods. Then we are using the PV cell solar cells and now we are going to use for the solar cells also.

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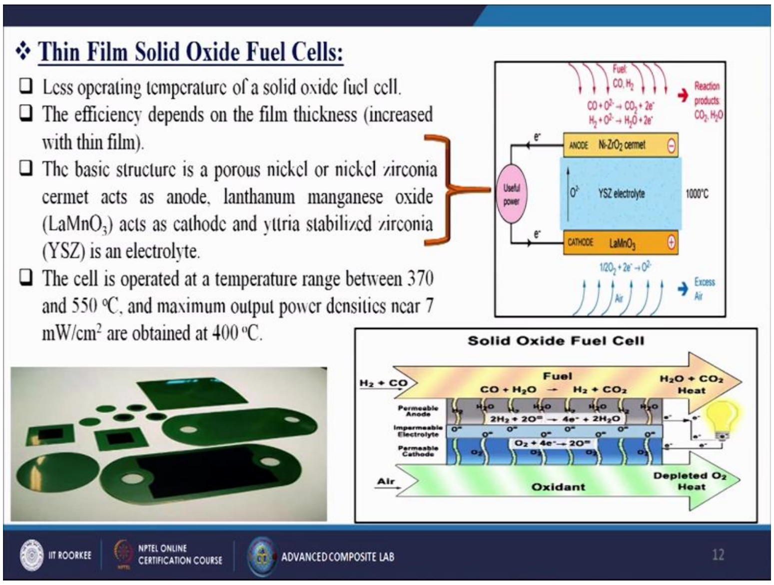

Then we are going to discuss about the thin film solid oxide fuel cells. So, it is a one kind of storing systems. Rather we can say it: less operating temperature of solid oxide fuel cells, the efficiency depends on the flame thickness increased with thin flame. Now this is also one of the hot topics, because as the days is going on going on going on our coal or maybe some kind of conventional things like our coal or maybe some kind of petrol, petroleum products are quantity is getting decreased. So, people are now thinking for the non conventional energy, like solar, like water, or maybe some kind of other things.

So, when you are talking about these materials, so these types of coatings are very very useful where we can use this kind of materials for generation of electricity for the future application, storing of the electricity, where we do not need any kind of conventional energy. So, the basic structure is a porous nickel or nickel zirconia cermets acts as anode, lanthanum manganese oxide act as cathode and yttria stabilized zirconias is an electrolyte. Here, we are using the anode then cathode and in between we are using the yttria stabilized zirconia. Then the cell is operated at a temperature range between 370 degree to 550 degree centigrade and maximum output power densities near 7 megawatt per centimeter square are obtained at 400 degree centigrade.

So, this is the output of those particular fuel cells. Here this is how it is acting it has been given over here, so the energy it is going from this one and it is glowing the valve over there and it is the continuous process for doing this kind of operations.

So, now we are going to discuss about the electrochromic and thermochromic coatings.

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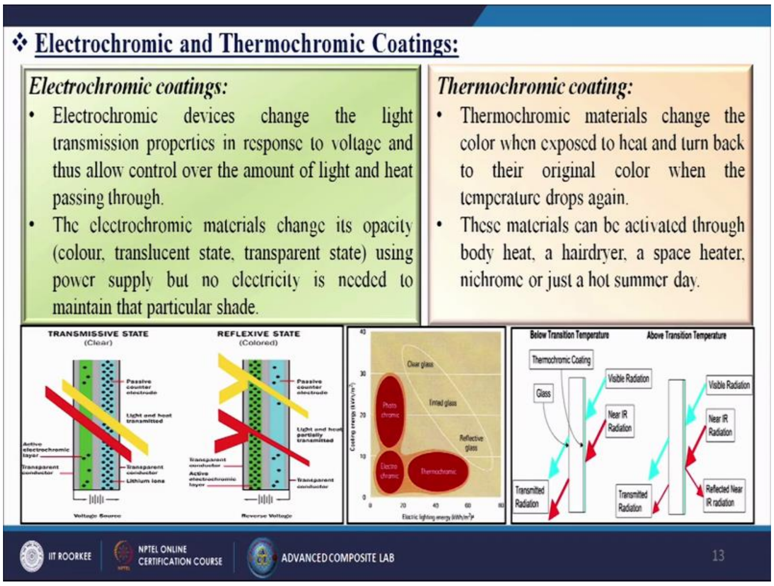

So, electrochromic coatings generally where we are using the light and heat some kind of voltage so that the light and heat can pass through or maybe when we are applying that voltage that light or maybe the heat will be reflected by this kind of materials. And we are using some kind of thermochromic coatings where with that temperature the automatically the properties of that particular materials will be changing.

If we remember that we are having some kind of specs, where in the sunlight it will automatically be came into the black color, but when you will enter into some cold room or maybe the cold temperatures so automatically it will become that transparent. So that kind of materials is coming under the thermochromic coatings. And electrochromic coatings is something like that, here we are having some layers the green one is called from active electrochromic layer. So, when we are introducing certain kind of potential difference in between that it is creating a barrier so that any kind of light or may be heat will not pass through it will be reflected through this material.

Next we are going to discuss about the permeation barriers. So, generally we are using this kind of materials for the barrier applications.

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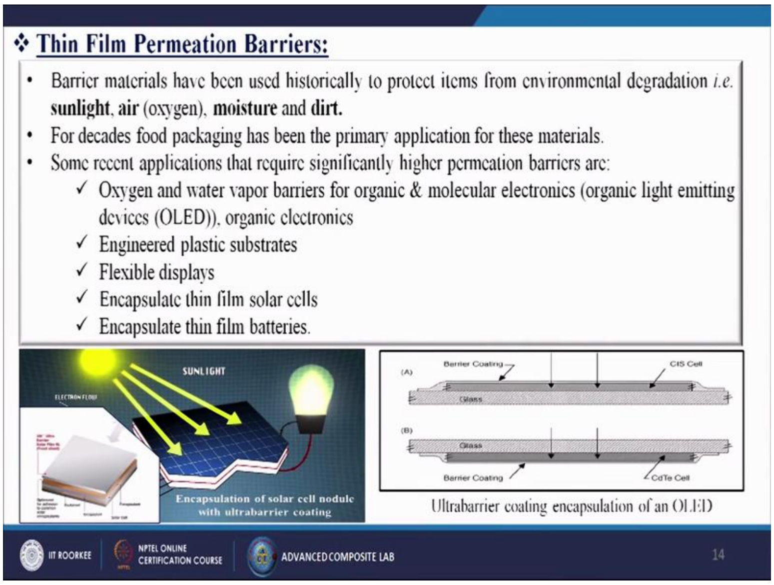

So, barrier materials have been used historically to protect items from environmental degradation, like sunlight, air, moisture, and dirt. So what are the applications? Some recent applications are that require significantly higher permission barriers are oxygen and water vapor barriers for inorganic and molecule electronics, engineer plastic substrates, flexible displays, encapsulate thin film solar cells, encapsulate thin film batteries. So here, we are doing these kinds of coatings for getting this kind of properties.

Next we are going to discuss about the photolytically driven electrochemistry. So, here generally this kind of materials we are using for the hydrogen storage, water splitting, generation of the hydrogen and oxygen for different materials.

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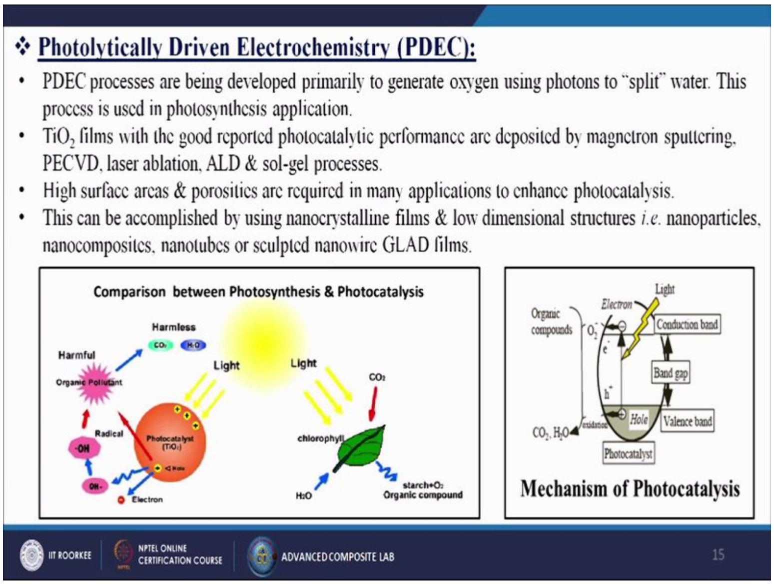

So, here we are using the titanium dioxide streams with the good reported photo catalytic performance are deposited by magnetron sputtering PECVD, laser ablation, ALD and the sol gel process. Not only that this can be accomplished by using nanocrystalline flames, low dimensional structures like nanoparticles, nanocomposite, nanotubes and or calculated nanoair GLD clings; so here these all of the applications. So, we are preparing certain kind of materials which is just like acting as leaps so that it can directly absorb the oxygen from the environmental itself, or maybe it can split the water so that the hydrogen and oxygen can be divided into two parts.

Next we are using this kind of materials from medical and hygienic applications.

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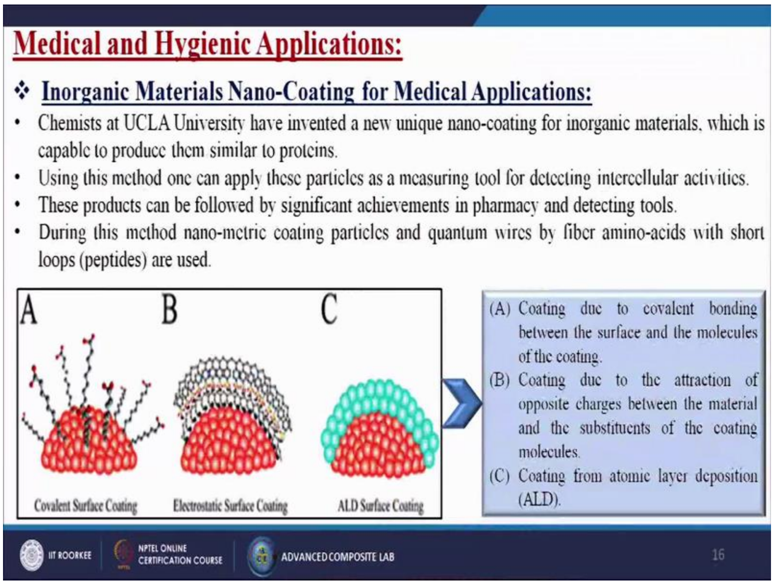

So, generally we are using this kind of materials for the antibacterial applications. So, chemists at UCLA University have invented new unique nano-coatings for inorganic materials which is capable to produce them similar to coatings. So, these materials are having wonderful properties like the biomedical applications. So, we are trying to develop the artificial coatings in our lab by doing this kind of coatings onto the surface.

Here, from this particular figure you can understand that; A is the coating due to covalent bonding between the surface and the molecules of the coating. Then B is the coating due to the attraction of opposite charges between the material and the substituents of the coating molecules. And C is the coating from atomic layer deposition. So, here we are going to show you actually the different types of coating techniques by which we can change the material properties, we can use these materials for the biomedical applications.

Then we are using this kind of nanoparticles for the mask actually. So, when people are using into some toxic environments or maybe into some chemical labs or maybe some any chemical industries, so where we need certain kind of masks to prevent ourselves from this toxic gases we are trying to use this kind of masks where you are using some kind of nanoparticles.

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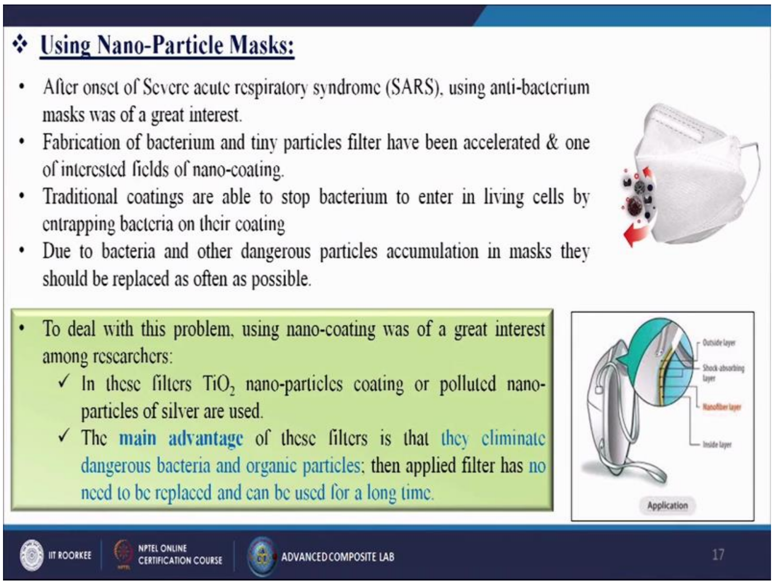

So, after onset of severe acute respiratory syndrome SARS using anti-bacterial marks was of a great interest, because nowadays there is a lot of smoke and the pollution is increasing in a higher rate. So, we are trying to save our life or maybe to inhale the good oxygen's, we are trying to use this kind of mask over there which will just give a barrier in between the toxic gases or maybe the carbon dioxide to inhale in our body. So, traditional coatings are able to stop bacterium to enter in living cells by entrapping bacteria on their coatings. Not only that it will trap only the toxic gases simultaneously it will trap the bacteria and viruses which is floating on the air.

Due to bacteria and other dangerous particle accumulations in musk they should be replaced as often as possible. So, how this materials is working? In these filters titanium dioxide nanoparticles coating or polluted nanoparticles of silver are used. The main advantage of these filters is that they eliminate dangerous bacteria and organic particles; then an applied filter has no need to be replaced and can be used for a longer time. So, easily we can clean those filters and we can use it for several times.

Next we are going to discuss about the hydroxyapatite nano coatings to design processes. So, in this particular case actually we are using these kinds of materials for our joint replacement, bone replacement, or maybe any kind of modifications in our body structure.

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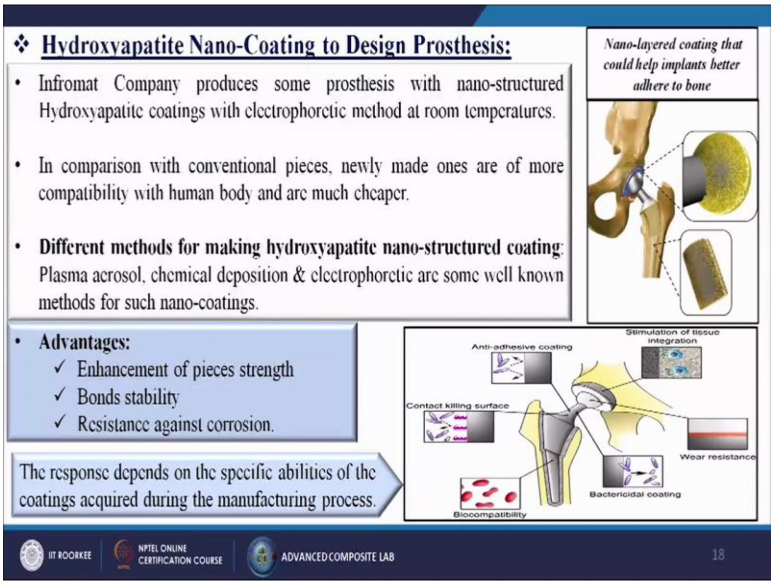

So, Informant Company produces some processes with nanostructure hydroxyapatite coatings with electrophoretic method at room temperatures. So, here we are using this kind of materials for our knee replacements or we can use it these kinds of materials for antiadhesive coatings, stimulation of tissue integrations, wear resistance, bacterial coatings, biocompatibility and contact killing surface. So, these materials are having wonderful applications for the biomechanical point of view. So, different method for making hydroxypatite nano-structured coatings: Plasma aerosols, chemical depositions, electrophoretic are some well known methods for such nano-coatings.

What are the advantages? Enhancement of piece strength, bond stability, resistance against corrosion; the response depends on the specific abilities of the coatings acquired during the manufacturing process. So, these are the properties generally we can incorporate into that material so that it can easily make a compatible with our body or maybe the inside our body liquid.

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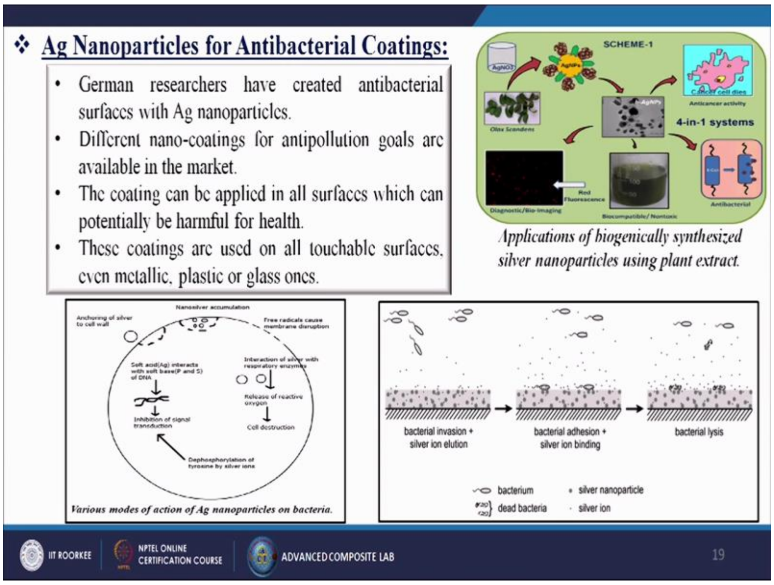

Next, some materials we are using for the antibacterial coatings like silver nanoparticles. So, here some researchers from the Germany, they have developed these kind of materials. So, different nano coatings for antipollution goals are available in the market. The coatings can be applied in all surfaces which can potentially be harmful for health. These coatings are used for all touchable surfaces and metallic plastic and glass ones.

So, here we are going to show you that different nanoparticle for different applications. So, we are using these materials for the cancer cell dies anticancer activity, so we can incorporate those materials into the body. So, it can directly go out onto the affected zone and it can kill the cancer cell over there. It is having some antibacterial properties, it can kill the bacteria inside our body, it is very very biocompatible and non toxic materials, then we are using these materials for the bioimaging specially for the targeted drug delivery so that from outside easily we can trace that where our medicine is going to the actual affected area or not.

Then, here we are going to show you that how the bacteria is coming with the contact over there and how the bacteria is killing. So, here the battery is coming we are having that coating first it is touching with that materials, first that is why it is known as the bacterial invasions and self aligned elution. Second is bacterial additions and silver ion bindings and after that the bacterial lyses. So, the bacteria is killing over there. So, this kind of materials is a very very fantastic material for the antibacterial applications.

So, now I am going to summarize my whole lecture into some brief points.

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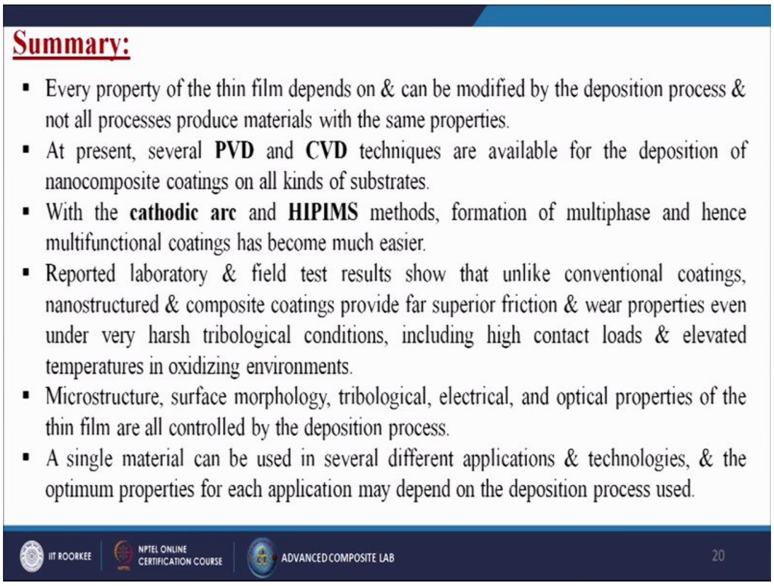

So, every property of the thin claim depends on or can be modified by the deposition process, and not all process produced materials with the same properties. At present several PVD and CVD techniques are available for the depositions of nanocomposite coatings on all kinds of substrates. With the cathodic arc and HIPIMS methods, formation of multiphase and hence multifunctional coatings has become much easier. So, a single material can be used in several different applications technologies and the optimum properties for each application may depend on the deposition process used.

So, the main motto of these particular things is that I have shown that different applications, but still the applications are very very few. There are thousands of applications where we are using these kind of coatings and not only that a single material will only can be used for one applications, a single materials can be used for various applications; not only that, by changing its outside coatings a single material can be used for different applications also. So, this is the whole conclusion of this particular chapter.

Thank you.